

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
18 April 2002 (18.04.2002)

PCT

(10) International Publication Number  
**WO 02/30861 A2**

(51) International Patent Classification<sup>7</sup>: C07C 51/215,  
53/08, 57/05

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(21) International Application Number: PCT/US01/31320

(22) International Filing Date: 4 October 2001 (04.10.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
60/239,449 11 October 2000 (11.10.2000) US

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(81) Designated States (national): AE, AG, AL, AM, AT, AU,  
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CZ,  
DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM,  
HR, HU, ID, IL, IN, IS, JP, KE, KG, KR, KZ, LC, LK, LR,  
LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ,  
NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM,  
TR, TT, TZ, UA, UG, US, UZ, YU, ZA, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM,  
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian  
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European  
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,  
IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF,  
CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD,  
TG).

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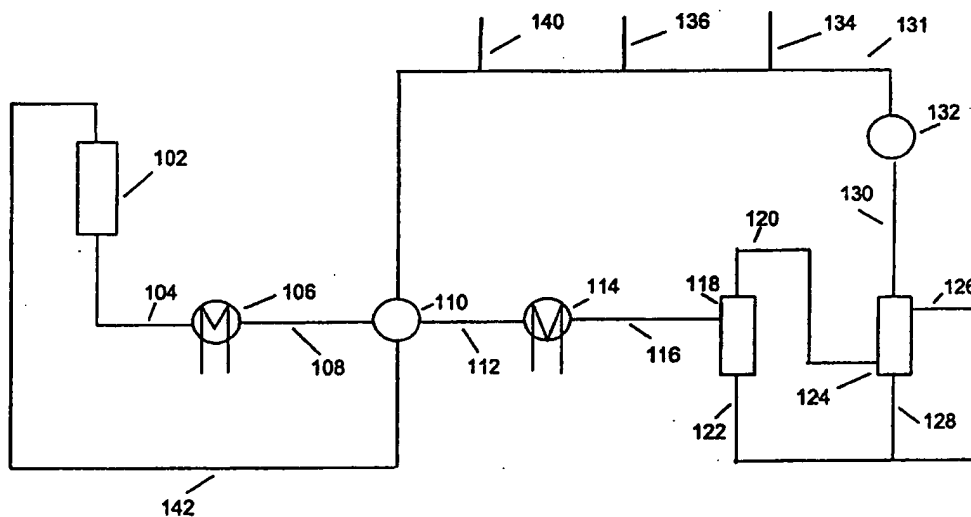
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Published:

— without international search report and to be republished  
upon receipt of that report

[Continued on next page]

(54) Title: PROCESSES FOR OXIDIZING HYDROCARBYL MOIETIES TO CARBOXYLIC ACIDS AND ANHYDRIDES



(57) Abstract: Continuous processes are provided for the partial oxidation in the vapor phase over a heterogeneous catalyst in a reaction zone of hydrocarbyl reactant to produce carboxylic acids or anhydrides wherein at least a portion of unreacted hydrocarbyl reactant is returned via a cyclic loop to the reaction zone. The partial oxidation generates carbon oxides which are used as ballast gas in the cyclic loop. The carboxylic acids or anhydrides are removed from the cyclic loop by condensation. Purification of the products can be by stripping lights and then dehydrating the carboxylic acid or anhydride product removed from the cyclic loop.

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PROCESSES FOR OXIDIZING HYDROCARBYL MOIETIES TO CARBOXYLIC  
ACIDS AND ANHYDRIDES

This invention pertains to continuous processes and apparatus for the partial,  
5 vapor phase, catalytic oxidation of reactant containing hydrocarbyl moieties to carboxylic  
acids and anhydrides (herein referred to as "carboxy compound"), especially lower saturated  
and unsaturated carboxylic acids and anhydrides. The processes use a cyclic loop in which  
unreacted hydrocarbyl moieties from the reactor are recycled to the reactor ("cyclic loop").  
In the processes of this invention, carbon oxide is used as a ballast gas. Liquid containing the  
10 sought carboxy compound is condensed from the cyclic loop and removed for purification.  
A subsequent aqueous absorption step in the cyclic loop can be used to remove additional  
amounts of carboxy compound. In a further aspect, the invention pertains to processes for  
the purification of carboxy compound withdrawn from the cyclic loop.

The partial oxidation of alkanes to carboxylic acids has long been proposed.  
15 U.S. Patent No. 2,800,504 discloses the catalytic, liquid phase oxidation of C<sub>4</sub> to C<sub>8</sub>  
hydrocarbons to aliphatic acids. A cyclic reaction system is disclosed wherein the oxidation  
product, which is a gas/liquid mixture, is cooled, waste gases purged in a first separator, and  
then a liquid/liquid separation is effected to recover an aqueous, carboxylic acid-containing  
bottoms layer and an upper hydrocarbon-containing layer which is returned to the reactor.  
20 The aqueous, carboxylic acid bottoms layer is dehydrated in a distillation column with the  
bottoms fraction containing a carboxylic acid product which may be subjected to further  
refining and an overhead fraction containing water which can be recycled to the reactor. The  
primary carboxylic acid product is disclosed as acetic acid when a butane feed is used.  
Hence, the reaction effects a cracking of the hydrocarbon. The purged gas from the first  
25 phase separator would likely contain unreacted oxygen as well as gaseous oxidation such as  
carbon monoxide and carbon dioxide.

Another process for the liquid phase oxidation of C<sub>4</sub>-C<sub>8</sub> hydrocarbons is  
disclosed in U.S. Patent No. 2,926,191. This process appears to be an improvement to the  
process disclosed in the 2,800,504 patent. The process involves the additional step of  
30 subjecting the aqueous bottom phase from the liquid/liquid separator to distillation to remove  
light ends. The light ends are cooled to condense, recover and recycle light organic  
materials.

U.S. Patent No. 2,801,259 discloses the vapor phase partial oxidation of hydrocarbons. The patentee theorizes that an equilibrium between acetic acid on the one hand and carbon monoxide and hydrogen on the other hand exists, and that acetic acid production can thus be favored by adding hydrogen and carbon monoxide to the reactor feed  
5 and by operating the oxidation reaction at higher pressures. The disclosed separation system results in the product stream from the reactor being cooled and subjected to a liquid/liquid phase separation. The organic layer is then scrubbed with water to remove further product and the overhead from the scrubber which may contain hydrogen, carbon monoxide, carbon dioxide and light hydrocarbon can be returned to the reactor.

10 U.S. Patent No. 3,646,128 discloses the non-catalytic oxidation of butane in the liquid phase to obtain methyl ethyl ketone. Acetic acid is noted by the patentees as being for the principle product of the vapor phase and liquid phase oxidation of butane. They state that the removal of carbon monoxide, carbon dioxide and water from the unreacted butane being recycled to the reactor results in an increase in the total productivity of the process. In  
15 the disclosed process, the reactor effluent is cooled, lights such as nitrogen, carbon monoxide and carbon dioxide are separated and vented from the system, and the remaining liquid is subjected to liquid/liquid phase separation. The organic phase is then further treated prior to being returned to the reactor. The treatment may be a caustic tower for carbon dioxide removal, a drying column for water removal and an extraction column for the removal of  
20 methyl ethyl ketone.

U.S. Patent No. 3,646,078 discloses the partial oxidation of higher alkanes and relates that the non-selective oxidation attacks the internal carbons. The patentees propose the use of a reactive diluent to provide a coordinated single liquid phase. In discussing the oxidant, the patentees recite that the dilution of oxygen with materials other  
25 than nitrogen is a worthwhile consideration and that carbon dioxide has particular attraction since at higher pressures such as 250 p.s.i.g. (17.2 bar), there appears to be a decarboxylation retardant effect. For batch operations, the patentees note that carbon dioxide can be deliberately added to the reaction environment at the start.

The catalytic oxidation of alkanes to unsaturated aldehydes and carboxylic  
30 acids such as acrolein, methacrolein, acrylic acid and methacrylic acid have received attention. U.S. Patent No. 4,066,704, for instance, discloses a catalytic oxidative

dehydrogenation process wherein the alkane is in the feed gas at a partial pressure of at least 0.70 atmosphere (0.71 bar) and the alkane constitutes more than 70 percent of the feed gas.

U.S. Patent No. 5,198,580 pertains to the oxidation of propane to produce acrylic acid among other products using a bismuth-containing oxidic solid catalyst. The patentees recite the use of diluents such as nitrogen and steam and say that the liquid products of the reaction can be separated from the unreacted feed hydrocarbons by condensation or scrubbing, usually by water or dilute acid.

U.S. Patent No. 5,380,933 discloses a molybdenum-containing catalyst for producing unsaturated carboxylic acids by the vapor phase oxidation of alkane. The use of an inert diluting gas such as nitrogen, argon and helium, and steam is a suggested adjuvant to enhance selectivity. The patentees state that the purity of the alkane feed is not particularly limited and mention that methane, ethane, air or carbon dioxide may be present in the alkane without any particular problem.

U.S. Patent No. 5,705,685 discloses the use of heteropolyacid or polyoxoanion catalyst for the oxidation of alkanes to unsaturated carboxylic acids. This reaction is stated to be preferably carried out in the vapor phase, and an inert gas such as nitrogen, argon or helium may be present.

U.S. Patent No. 5,750,777 also relates to the oxidation of alkanes to carboxylic acids using a catalyst comprising vanadium, titanium, molybdenum, phosphorous and oxygen. In describing the process, the patentees state that the acid formed is separated, conventionally by cooling and then condensing an acid/water mixture.

U.S. Patent No. 3,555,083 discloses a process for the purification of carboxylic acids made by the oxidation of alkanes. In the disclosed process, the oxidized product is first passed to a distillation column to remove high boiling point residues then to a dehydrating column. The bottoms fraction from the dehydrating column is further rectified to remove formic acid. The overhead from the dehydrating column contains light organics which aid in enhancing water.

PCT Published Patent Application 97/36849, October 9, 1997, discloses a process for the oxidation of alkanes including the oxidation of propane to acrylic acid. The oxidation is said to proceed stepwise with the conversion of, for instance, propane to propene which in turn is converted to an unsaturated aldehyde (acrolein) which is then further oxidized to acrylic acid. The applicant contemplates the recycling of unreacted

alkane which may be accompanied by carbon oxides since the oxydehydrogenation catalysts that the applicants prefer to use are substantially unaffected by carbon oxides and water. The applicant further contemplates the combination of some of the oxidation steps in a single reactor. The applicant states at page 9, lines 9 to 11, that it may also be possible to conduct  
5 both the propane-to-propylene and the propylene-to-acrolein reactions in a single reactor with one or more stages.

The oxidation of alkanes to produce saturated and unsaturated carboxylic acids has thus been a long developing art. Nevertheless, the conventional process for producing acetic acid is via the carbonylation of methanol, and oxidation, including oxidative  
10 dehydrogenation, of alkanes perhaps has not yet met with its full commercial potential. Accordingly, a need exists to provide improved vapor phase oxidation processes that offer the potential for a given catalyst, that have advantaged investment and operating costs.

In accordance with this invention, improved vapor phase processes for the catalytic oxidation of reactant containing hydrocarbyl moieties to carboxylic acids and  
15 anhydrides ("carboxy compound") are provided. The processes and apparatus of this invention use a carbon oxide ballast gas in a cyclic loop. A substantial amount of the carboxy product generated is removed by condensation. It has been found by this invention that the use of a by-product of the reaction, carbon oxides, as the ballast for the continuous, cyclic process does not unduly affect the kinetics of the reaction or the carboxy compound  
20 separation system. The advantages provided by the use of carbon oxides as the ballast include the ability to operate the reaction system at oxygen concentrations below the flammability limit yet preferably conduct the process using a single reactor. Heretofore, in order to obtain economically viable conversion of hydrocarbyl moieties to carboxy compounds, the common practice has been to use multiple reactors with oxygen injection  
25 between reactor stages so as to maintain the oxygen concentration in any single reactor below the flammability limit. Another advantage of this process is that, if desired, carbon oxide by-products can be removed via a purge from the cyclic loop and, thus, no expensive separations systems may be required for this purpose. Thus the processes of this invention can be conducted with few unit operations and thus provide desirable investment economics.  
30 A further advantage of the processes of this invention is provided by the higher heat capacity of carbon oxides than common, essentially inert ballast gases such as

nitrogen. The exothermic, partial oxidation reaction can be more facily be controlled to prevent temperature excursions, even on a localized basis within the reactor.

If desired a subsequent aqueous absorption step in the cyclic loop is conducted to remove additional amounts of the carboxy compound. Hence, in combination  
5 with the amounts of carboxy compound removed by condensation, it is readily apparent that the product can be efficiently removed from the cyclic loop. This aqueous absorption will also remove some of oxidation by-products contained in the fluid being recycled in the cyclic loop. The recovery of these oxidation by-products can reduce the amount of purge necessary to maintain suitable concentrations of these components in the cycling stream.

10 In an advantageous aspect of the processes of the invention, the composition of the purge stream may be sufficiently high in fuel value that it can be used as fuel, for example, in steam boilers. Especially where an alkane hydrocarbyl reactant is used, the purge does not significantly detract from the economic attractiveness of the processes of this invention since the cost differential between the value of the alkane as a feed stock and the  
15 value as a fuel is relatively small.

In the broad aspects of the invention, continuous processes for catalytically oxidizing a hydrocarbyl moiety ("hydrocarbyl reactant") to carboxylic acid or anhydride ("carboxy compound") in which processes unreacted hydrocarbyl reactant is recycled in a cyclic loop is provided which comprises:

- 20 a) continuously contacting in a vapor phase a gaseous mixture comprising containing hydrocarbyl reactant, an oxygen source and carbon oxides in the presence of a catalytically effective amount of a heterogeneous oxidation catalyst, under oxidation conditions to produce an effluent gas which contains carboxy compound and unreacted reactant and carbon oxide, wherein carbon oxides comprise at least 30 percent by  
25 volume of said gaseous mixture;
- b) cooling said effluent gas to condense at least 50, preferably at least 70, percent of the carboxy compound and separating the condensed phase;
- c) optionally continuously contacting the gaseous phase from the separation of step (b) with an aqueous absorbent said contacting being under conditions of  
30 temperature and pressure such that the aqueous absorbent selectively absorbs said carboxy compound as compared to said unreacted reactant, thereby producing a carboxy compound-depleted gas;

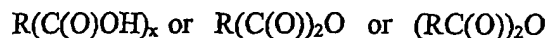
- d) continuously recycling the effluent gas in the cyclic loop to step (a);
- e) at least periodically withdrawing a purge from the cyclic loop said purge being in an amount sufficient to maintain steady state operation of the process; and
- f) at least periodically adding to the cyclic loop sufficient amounts of hydrocarbyl reactant and oxygen to maintain steady-state operation.

In another broad aspect of the processes of this invention, the continuous processes for the catalytic oxidation of hydrocarbyl reactant to produce carboxy compound comprises (a) reacting a hydrocarbyl reactant with an oxygen source in the presence of oxidation catalyst under oxidation conditions to produce a carboxy compound, carbon oxides and water; (b) separating said carboxy compound to provide a carboxy compound-rich stream and a carboxy compound-depleted stream; (c) recycling at least a portion of the carboxy compound-depleted stream to step (a); and (d) recovering carboxy compound from the separated carboxy compound-rich stream, are improved by:

- i) passing said separated carboxy compound-rich stream to a first distillation zone to produce a bottoms stream comprising less than 0.5 volume percent carbon oxides, and an overhead stream containing carbon oxides,
- ii) passing the bottoms stream from the first distillation zone to a dehydration zone to produce a stream containing carboxy compound which stream is reduced in water content, preferably to less than 20 weight percent water. Often this dehydration can be effected via a distillation. If the carboxy compound azeotropes with water, in some instances, the water content of the stream containing carboxy compound is less than that required to form the azeotrope.

Figures 1 and 2 combine to form a schematic depiction of an apparatus for use in conducting the processes of this invention to produce acrylic acid. Figures 1 and 3 combine to form a schematic depiction of an apparatus useful in conducting the processes of this invention to produce acetic acid.

The processes of this invention pertain to the oxidation of compounds containing hydrocarbyl reactant to carboxy compounds in a cyclic loop, gas phase reaction system using a carbon oxides-containing ballast gas. The carboxy compounds include carboxylic acids and anhydrides and may be saturated or unsaturated. Often the carboxy compounds can be represented by the formulae





wherein R is a substituted or unsubstituted aliphatic or aromatic moiety having at least one, say, one to twenty, frequently one to ten carbons and x is an integer from one to six, most often from one to four. R may contain, besides hydrogen, hetero atoms such as phosphorus, nitrogen, sulfur and halogen such as chlorine, fluorine and bromine. When R is an aromatic moiety the structure may be monocyclic or polycyclic, including by fused rings. In many instances, the carboxy compounds made in accordance with this invention have a molecular weight of less than 500, frequently less than 250, and contain two to ten carbon atoms. In the carboxy compounds that are anhydrides, the carboxy groups are on vicinal carbons of R. Preferably R is lower alkyl or lower alkylene of one to four carbon atoms or monocyclic aryl or aralkyl of 5 to 8 carbon atoms.

Representative carboxy compounds include acetic acid, chloroacetic acid, malonic acid, propionic acid, acrylic acid, n-butyric acid, isobutyric acid, methacrylic acid, acetic anhydride, ethylenediaminetetraacetic acid, adipic acid, succinic acid, hydroxysuccinic acid, succinic anhydride, maleic acid, maleic anhydride, phthalic anhydride, phthalic acid, terephthalic acid, benzoic acid, hexahydroxybenzoic acid, toluic acid, and valeric acid.

The reactants used for producing the carboxy compounds have hydrocarbyl moieties that can be oxidized to the corresponding acid or anhydride. The hydrocarbyl moieties are preferably primary, that is, have three hydrogens. Thus, the reactants may be represented by the formulae:  $R(CH_3)_x$ , wherein R and x are as defined above, however, it is generally preferred that the carbon atom bonded to the hydrocarbyl moiety either be a member of an aromatic ring or saturated. The processes of the invention are particularly useful in the conversion of alkanes to saturated and unsaturated carboxylic (including dicarboxylic) acids and anhydrides. Under some conditions, dehydrogenation occurs during the oxidation to produce an unsaturated carboxy compound. For instance, butane may be useful as a reactant to produce succinic anhydride. In preferred aspects of the process, the hydrocarbyl reactant is an aliphatic or aromatic hydrocarbon of 2 to 10, preferably 2 to 8 or even 2 to 5, and often 3 to 5, carbon atoms.

The processes of the invention are conducted under oxidation conditions in the gas phase in the presence of a heterogeneous catalyst. The reactive oxygen for the reactor may be provided by any suitable source, and molecular oxygen is conveniently used, either as a purified oxygen feed or air. In practice, the reactive oxygen is introduced into the cyclic loop separately from the hydrocarbyl reactant.

The amount of reactant in the gases passing to the reactor can also be selected over a wide range. Because hydrocarbyl reactant is recycled in the cyclic loop, it can be present in a substantial excess of that stoichiometrically required for reaction with the oxygen without any material deleterious effect on the economics of the process. In general  
5 practice, the hydrocarbyl reactant is maintained in a substantial stoichiometric excess to provide a high partial pressure relative to that of the oxygen reactant to favor the reaction kinetics to the carboxy compound products. Often the hydrocarbyl reactant comprises from 5 to 50, say, 10 to 40, volume percent of the total feed to the reactor.

Of the amount of the hydrocarbyl reactant that is fed to the reactor, less than  
10 50 percent, and usually less than 30 percent, is reacted in a single pass through the reactor. The extent of the hydrocarbyl reactant consumed per pass through the reactor will depend, in part, upon the amount of heat generated by the reaction that can be dissipated, for example, through heat exchange during the reaction, and the increase in temperature that can be tolerated in the reactor.

15 The high concentration of carbon oxides recycled to the reactor results in an ability to use a greater amount of oxygen without forming an explosive mixture. The mole ratio of oxygen atoms fed to the reactor is frequently below 30, preferably below 20, percent of that required to react with the reactant on a stoichiometric basis to produce the sought carboxy compound. Of the oxygen fed to the reactor, typically at least 60, and sometimes at  
20 least 90, percent of the oxygen is consumed per single pass. The gases in the cyclic loop generally contain less than 5 volume percent, and sometimes less than 2 volume percent, free oxygen based upon the total volume of reactor effluent.

The amount of carbon oxides fed to the reactor as the ballast gas can be selected over a wide range. Generally, the carbon oxides are at least 30 volume percent of  
25 the gases fed to the reactor. Often carbon oxides comprise 30 to 90, preferably 50 to 90, volume percent of the gases fed to the reactor. The selection of the amount of carbon oxides used as the ballast gas in the cycle loop is an economic trade-off. At lower levels, the purge stream will contain a higher proportion of unreacted hydrocarbyl reactant, and at higher levels, more energy will be consumed in recycling the gases. Advantageously, the carbon  
30 oxides, especially carbon dioxide, present during the reaction serve as a heat sink to aid in control of the oxidation reaction.

The gases passing to the reactor, in addition to oxygen, hydrocarbyl reactant and carbon oxides, may contain other adjuvants such as ancillary ballast gases, for example, nitrogen, and gas phase promoters for the catalysts. Impurities may also exist such as argon which may be present with an oxygen feed. If air is used as the oxygen-containing feed,  
5 nitrogen will be present. Also, other oxidation products will typically exist such as aldehydes and ketones.

The carbon oxides comprise carbon dioxide and optionally carbon monoxide. Carbon monoxide is a by-product of the oxidation reaction. For catalyst systems that are not unduly adversely affected by the presence of carbon monoxide, the volume ratio of carbon  
10 monoxide to carbon dioxide in the gases being passed to the reactor is often 0.7:1 to 1.5:1. For catalysts such as those comprising gold or palladium, carbon monoxide can act as a catalyst poison. In those instances it is preferred to eliminate carbon monoxide from the cycle gases prior to their being reintroduced into the reactor. Often, under these circumstances, the amount of carbon monoxide being fed to the reactor is less than 100  
15 ppmv (parts per million by volume) of the total gases. The carbon monoxide elimination may be by sorption or oxidation.

Water will be present in the gases passing from the reactor due to the reaction and because of the equilibrium established between the cycle fluids in the loop and the contact with the aqueous sorption media used to remove carboxy compound products.

20 The reactor may be any suitable reactor for heterogeneous catalysis. Because of the exothermic nature of the oxidation reactions, it is generally preferred to use a reactor design that enables the removal of heat during the reaction. One type of reactor design which has found use in exothermic processes is the tubes in a shell reactor wherein the catalyst is contained in the tubes and a heat transfer fluid (for example, water, oil, or gas) is  
25 provided as a heat transfer fluid at the exterior of the tubes. Other reactor designs such as moving bed and fluidized bed can be used. In some instances, it may be desired to introduce a vaporizable liquid into the reactor to provide cooling upon vaporization. The liquid may be condensed hydrocarbyl reactant or an inert.

The oxidation conditions used in the processes of this invention provide the  
30 oxidation of the hydrocarbyl reactant to the sought carboxy compound. The conditions include the use of an elevated temperature and the presence of catalyst. The selection of the pressure used will be influenced by a number of factors including: assuring that the effluent

fluid from the reactor is substantially gaseous, maintaining the partial pressure of oxygen below the flammability limit, and providing partial pressures of the reactants that enhance the reaction rate to carboxy compound. Often, the pressure is between 0.1 to 100 bar absolute, say, between 1 to 50 bar absolute. In many instances, a pressure between 4 and 30 bar absolute provides an economic balance among reaction rate, energy consumption, construction costs while maintaining the composition of the feed to the reactor below the flammability limit.

The temperature selected for the reaction may fall within a wide range and will depend upon the catalyst used and the relative reaction rates to undesired by-products. Often the temperature is between 150°C. to 700°C., say, between 225°C. to 550°C.

The catalyst employed in the processes of this invention is a heterogeneous, preferably solid, catalyst suitable for the oxidation of hydrocarbyl reactant to the corresponding acid or anhydride. Among the oxidation catalysts are supported and unsupported catalysts containing one or more metals, oxides or salts of Group IVb, Group Vb, Group VIb, Group VIIb, Group VIII, Group Ib and Group IIb elements and the rare earth elements, especially Lanthanides, such as cerium. When supported, the supports are preferably do not promote undesirable reactions under the conditions of the reaction and may be substantially inert. Included among the supports include alumina, particularly alpha alumina, although gamma, beta and other transition phase aluminas can be used, silicas, solgels, titania, aluminosilicates including zeolitic structures and molecular sieves, and other mixed oxide structures including layered clays, tungstoaluminas.

Mixed oxide catalysts have found particular utility in the processes of this invention, in part, because of their general lack of sensitivity to carbon oxides, including carbon monoxide. Exemplary catalysts include supported and unsupported Group Vb and VIb metal oxides such as oxides of one or more of vanadium, niobium, molybdenum and tungsten. These catalysts may also contain alkali or alkaline earth metals or compounds, especially sodium, potassium and cesium. Group VIIb metal oxides may also be provided. Oxides of manganese and rhenium have found particular application. Although the above catalyst components have been described in terms of oxides, it should be well appreciated that the components may be provided in any convenient form including in elemental or salt form, which may converted to oxide or other form during the course of use. It should further be recognized that although the components have been characterized as oxides, they

might be in a different chemical form under reaction conditions. The term oxide as used herein is thus intended to cover all such forms regardless of whether or not the metal is actually an isolatable oxide in the catalyst.

Most frequently the catalysts are formed as cogels or as precipitates. They  
5 may be supported, if desired, and the supports are aluminas (including alpha, beta, theta, gamma and other transition aluminas), silica-aluminas, titania-aluminas and niobia. The size of the catalyst particle may vary widely and may be monolithic, such as honeycomb structures, or particulates, say of 0.05 to 25 millimeters in major dimension. The catalyst particles may be porous or relatively non-porous.

10 Often the catalysts contain molybdenum, and some may be described by the elemental formula (not including any inert support):



wherein A is one or more of sodium, potassium, calcium, magnesium and cesium; Mo is molybdenum; D is one or more of vanadium, manganese, niobium, tungsten  
15 and rhenium; E is one or more of cerium, lanthanum, aluminum, titanium, antimony, bismuth, phosphorus and silicon; O is oxygen; a is 0 to 5, preferably 0.1 to 2; m is 0 to 12; d is 0 to 10, preferably 0.1 to 5; e is 0 to 10 and x is a number to satisfy the valencies of the catalyst. When supported, the above elemental components are provided in an amount of 0.5 to 50 weight percent of the total weight of the supported catalyst.

20 The processes of this invention employ a cyclic loop for the return of unreacted hydrocarbyl reactant to the reactor. From the cyclic loop, a product-containing stream is withdrawn and a purge is taken to provide substantially steady state operation. The purge is usually taken after the product removal so as to minimize the loss of the carboxy compound. The amount of the purge will depend, as stated above, the level of carbon oxide  
25 ballast sought for the cyclic loop. Advantageously, the purge from the processes of this invention has a sufficiently high combustible component content that it can be used for fuel. The combustible components in the purge can include carbon monoxide and unreacted hydrocarbyl reactant. Especially in embodiments where the hydrocarbyl reactant is an alkane such as ethane or propane, the value of the alkane as fuel is a substantial portion of its value  
30 as a reactant.

The effluent from the reactor is cooled to remove the heat of reaction from the reaction system, and, as discussed below, is preferably cooled to a temperature sufficient

to condense out at least a portion of the carboxy compound. Preferably at least 50 percent of the carboxy compound removed, is removed by cooling the gases in the cycle loop to condense a liquid phase which will contain the carboxy compound. Often at least 70, and most preferably, at least 90, percent of the carboxy compound is removed by this

5      condensation. The advantage of removal by condensation is two-fold. First, the equipment to remove the carboxy compound can be relatively non-complex and, second, to the extent that supplementary carboxy compound removal is desired, the load on that equipment can be less. Often, the temperature for condensing the carboxy compound is between 20 and 150°C., say, 30 and 70°C., and the pressure is between 1 to 50, say, 4 to 30, bars absolute.

10              Advantageously, where the carboxy compound is unsaturated, cooling of the reactor effluent occurs immediately to avoid conditions which promote polymerization. In some aspects of the invention, the cooling occurs in two steps. The first step provides the quick cooling to minimize polymerization, and the second step provides the bulk of the condensation of the carboxy compound.

15              Supplementary separation may be used to remove additional amounts of carboxy compound product from the cyclic loop. The means selected for this supplementary separation will generally be chosen based upon the nature of the hydrocarbyl moiety-containing reactants and the carboxy compound products. Supplementary separation means include membranes, distillation, crystallization, liquifaction, extraction, adsorption and  
20      absorption.

A particularly attractive supplementary separation means is via aqueous absorption. Carboxy compounds are generally significantly more soluble in water than the hydrocarbyl reactants. The carboxy compound product may be in the liquid, gaseous or mixed phase in the fluid contacting the aqueous medium. The temperature and pressure of  
25      the absorption is sufficient to maintain the aqueous medium substantially in the liquid phase. Often, the temperature is between 20 and 150°C., say, 30 and 70°C., and the pressure is between 1 to 50, say, 4 to 30, bars absolute. Advantageously, where the carboxy compound is unsaturated, the temperature for the absorption is preferably below 50°C., and is frequently in the range of 20 to 40 or 45°C.

30              The amount of water in the aqueous medium is generally sufficient to absorb at least 50, preferably at least 75, say, 75 to 99, weight percent of the carboxy compound contained in the fluid contacting the aqueous medium. Preferably, the amount of hydrocarbyl

reactant sorbed into the aqueous medium is less than 10, more preferably less than 5, weight percent based on the weight of the carboxy compound sorbed. Water often comprises at least 70, and often at least 90, weight percent of the aqueous medium fed to the sorption. The aqueous medium may contain other components, either as impurities or as adjuvants to  
5 assist in the sorption or enhancing stability of the carboxy compound product when absorbed. Adjuvants may include pH adjusters and buffers. Often, the aqueous medium has a pH of between 3.5 and 9, say, 4 and 8. For carboxy compound products that are polymerizable such as acrylic acid, polymerization inhibitors such as phenothiazine, hydroquinone or the monomethyl ether of hydroquinone may be included, usually in the  
10 amount of between 1 to 500 parts per million by weight. Often, between 0.1 to 10, say 0.5 to 5, parts by weight of aqueous absorbent are used per part of carboxy compound absorbed.

The equipment used for the absorption of the carboxy compounds may be of any suitable design. For instance, the aqueous medium may be sprayed over an upwardly rising gas stream containing the carboxy compound products, or the aqueous medium may  
15 form a continuous phase through which the gases are bubbled, and the aqueous medium may be itself moving in a concurrent, countercurrent or cross-current direction to the direction of flow of the bubbles. If the stream containing the carboxy compound product is liquid, the absorption may be conducted as a liquid-liquid extraction process. The aqueous medium may be passed in a concurrent or countercurrent direction to the flow of the liquid.

20 The lean effluent from the sorption is returned to the reactor via the cyclic loop. After product recovery, the fluid in the cyclic loop can be reheated, for example, by indirect heat exchange with the warmer fluid in the portion of the cyclic loop following the reactor.

The carboxy compound removed from the cyclic loop can be processed to  
25 provide a refined carboxy compound. If a supplemental separation is employed, the streams from the condensation and the supplementary separation can be combined for purposes of the refining.

The oxidation reaction generally produces low boiling byproducts. A preferred process for the refining of the carboxy compound is to first subject the recovered  
30 carboxy compound to a stripping, or distillation, operation to provide a bottoms stream rich in water and the sought carboxy compound products and an overhead containing the light byproducts such as carbon dioxide and carbon monoxide. The overhead may also contain

the hydrocarbyl reactant if of sufficiently low molecular weight, for example, ethane, ethylene, propane and propylene. This overhead stream may have a sufficiently high fuel content to be used as fuel value.

5 The stripping column usually operates with a base temperature between 50 and 200°C and at a pressure sufficient to maintain water in the liquid phase, for example, between 0.2 to 10 bars absolute. Where the carboxy compound is subject to polymerization, preferably the base temperature is maintained sufficiently low so as to minimized undue polymerization, for example, between 50 and 120°C and at these temperatures, the pressure is often subatmospheric, say, between 0.2 to 0.9 bar absolute.

10 The bottoms fraction from the stripping column is then dehydrated by distillation. The conditions used in the dehydration column will be influenced by the stability of the sought carboxy compound, including whether or not the carboxy compound is subject to polymerization. For instance, if the carboxy compound is acrylic acid, it is generally preferred to operate the column with a base temperature below 110°C. Consequently, the  
15 base of the column is operated under vacuum, for example, between 0.1 and 0.95, say, between 0.2 and 0.8, bar absolute.

However, if the product is relatively free from unsaturated carboxy compounds such as would be the case if acetic acid were being produced, the base temperature of the column may be in the range of 120 to 200°C or more, and the column  
20 need not be operated under vacuum. The pressure in the dehydration column may be within the range of 0.5 to 20, say, 1 to 10, bars absolute.

Some carboxy compounds, such as acetic and acrylic acid, are difficult to separate from water. Consequently assisted or azeotropic distillation techniques are used. In azeotropic distillations, the overhead may comprise as little as 5, preferably at least 50, weight  
25 percent water.

The bottoms from the dehydration column that contain the carboxy compound can be further refined, for example, through distillation.

If an aqueous absorption is used as a supplementary separation system, the refining can be used to provide a water stream suitable to recycling to the absorber. It is not  
30 essential that the entire amount of the carboxy compound be removed from the aqueous medium being regenerated.



The invention will be further illustrated by reference to the drawings that pertain to a process for the oxidation of propane to produce acrylic acid. The description of the drawings is not intended to be limiting of the broad aspects of the invention.

- With reference to Figure 1, a propane-containing feed is reacted in reactor
- 5 102. The reactor is a tube in shell reactor using Dowtherm™ heat transfer fluid on the shell side, and the temperature of the gaseous effluent from reactor 102 is maintained at 350°C. through heat exchange cooling and adjusting the oxygen concentration and gas hourly space velocity. The catalyst is a cogel containing 0.4 weight percent sodium, 5 weight percent molybdenum and alumina in the form of pellets of nominally 5 to 7 millimeters in diameter.
- 10 The catalyst loading is 10 kilograms of reacted propane per kilogram of catalyst.

The gases exiting the reactor are at a pressure of 16 bars absolute. The effluent, for the purposes of this exemplification, has the following composition:

	Component	Volume Percent
	Carbon Dioxide	43.5
15	Carbon Monoxide	27.0
	Propane	15.8
	Water	9.0
	Acrylic Acid	3.3
	Oxygen	1.0
20	Other	0.4

- The effluent from reactor 102 is passed via line 104 to heat exchanger 106. While line 104 is depicted in the schematic representation, in normal practice, heat exchanger 106 is integral with the outlet of reactor 102 in order to minimize the time that the acrylic
- 25 acid-containing gases are at reaction temperature. Heat exchanger 106 generates steam at 14.8 bars absolute. The gases exiting heat exchanger 106 are at 250°C. The gases then pass via line 108 to heat exchanger 110 which is a countercurrent indirect heat exchanger using cooled gas in the cycle loop as the other heat exchange fluid as described later. This heat exchanger cools the gases to 122°C, and the cooled gases are passed via line 112 to heat
- 30 exchanger 114 which further cools the effluent to 40°C. A mixed phase system is present. This mixed phase fluid is passed via line 116 to separator 118 to provide a bottoms stream containing acrylic acid that is withdrawn via line 122 and a vaporous overhead. About 98.6 percent of the acrylic acid contained in the mixed phase fluid enter the bottom stream of separator 118.

In the depicted process, a supplementary separation system is employed to recover additional acrylic acid values. The use of a supplementary separator is not essential to the broadest aspects of the invention. Indeed, the portion of the acrylic acid recovered through condensation is quite high and can be increased, if desired, by lowering the temperature of the reactor effluent gases. The vaporous overhead from separator 118 is passed via line 120 to the bottom of absorber 124. The absorber contains sieve trays to promote gas-liquid contact. The lean absorption liquid enters absorber 124 via line 126. The lean absorption liquid which is essentially water contains the monomethyl ether of hydroquinone, a polymerization inhibitor. About 1.42 kilograms of water in the lean absorption liquid are supplied to absorb one kilogram of acrylic acid.

The spent absorption liquid is removed from the bottom of absorber 124 and is passed through line 128 and combined with the liquid in line 122 for recovery of the acrylic acid in the purification system further described in connection with Figure 2. This combined stream has a composition of:

Component	Weight Percent
Acrylic Acid	56.9
Water	37.6
Acetic Acid	2.9
Formaldehyde	1.1
Other	1.5

The scrubbing in absorber 124 is sufficient to reduce the concentration of acrylic acid in the absorber overhead to 100 parts per million by volume. The composition of the overhead is:

Component	Volume Percent
Carbon Dioxide	49.3
Carbon Monoxide	30.8
Propane	18.0
Oxygen	1.1
Water	0.6
Other	0.2

This overhead is passed to compressor 132 via line 130 where it is compressed from 14.5 bars absolute to 17 bars absolute. The temperature of the gases increases during the compression to 55°C. The compressed gases from compressor 132 are cycled to heat exchanger 110 via line 131.

Line 134 draws from line 131 a purge stream of 1.7 volume percent of the overhead from the absorber. Alternatively, the purge stream may be taken from line 130. The purge stream can be used as fuel, for example, for steam boilers.

Make-up propane and make-up oxygen are added to line 131 via lines 136 and 140 respectively. The oxygen is preferably high purity oxygen. The composition of the gas with the make-up propane and oxygen is:

10	Component	Volume Percent
	Carbon Dioxide	42.7
	Carbon Monoxide	26.7
	Propane	19.9
	Oxygen	10.0
	Other	0.7

In heat exchanger 110, the temperature of the cycling gases is increased to 187°C, and then the gases are fed to reactor 102.

With reference to Figure 2, the acrylic acid recovered from the cycle loop of the reaction system that is contained in line 122 of Figure 1 is passed to lites stripper column 202. In view of the potential for the acrylic acid to polymerize, the lites stripper column is operated with a head pressure of 0.56 bar absolute and a temperature of 82°C. The overhead which contains carbon dioxide, carbon monoxide and low boiling hydrocarbons and oxygenated hydrocarbons, is passed via line 204 to chiller 206 which drops the temperature to 10°C such that additional propane in the overhead is condensed. The mixed phase stream is then passed to separator 208 with the liquid phase being returned to the lites stripper column via line 212 and the gas phase being vented via line 210. The gas phase contains:

30	Component	Volume Percent
	Propane	47.7
	Carbon Dioxide	38.3
	Acetone	8.3
	Carbon Monoxide	2.1
	Other	3.6

The bottom temperature in lites column 202 is maintained at 90°C. Monomethyl ether of hydroquinone is provided to the top of lites column 202 as a polymerization inhibitor. The bottoms fraction from the lites column is passed via line 214 to dehydration column 216. The head pressure of the dehydration column is 0.55 bar absolute and the temperature is 60°C. Isopropyl acetate is used as a solvent to facilitate the

separation between water and acrylic acid. Other entraining agents such as butyl acetate and methyl isobutylketone may also find utility.

The overhead from dehydration column, which contains primarily water and isopropyl acetate, is cooled to 40°C and is decanted in vessel 217. The upper fraction is  
5 returned as reflux and the lower fraction is passed via line 218 to heat exchanger 220 which increases the temperature of the stream to 80°C. The heated stream is then passed via line 222 to solvent column 224 where isopropyl acetate is distilled from water. The head pressure in solvent column 224 is approximately ambient atmospheric pressure and the temperature is 93°C. The overhead from solvent column 224 is cooled to 40°C and  
10 decanted in vessel 226. The lower fraction is returned to the solvent column as reflux, and the upper fraction, which contains 97.5 weight percent isopropyl acetate and 2.5 weight percent water is returned via line 228 to dehydration column 216.

The bottoms fraction from solvent column 224, which is essentially water, is passed via line 250 through heat exchanger 220 where it is cooled from 100°C to 60°C. The  
15 stream is further cooled in heat exchanger 252 to 40°C and passed to splitter 254. Line 256 from splitter 254 serves to purge water from the system to maintain a steady state operation. This purge stream is typically sent to waste water purification. The other portion of this stream is returned via line 126 to absorber 124 on Figure 1.

Returning to dehydration column 216, the base temperature is maintained at  
20 97°C, and polymerization inhibitor (monomethyl ether of hydroquinone) is provided at the top. Under these conditions, water will still be present in the bottoms fraction. For the production of acrylic acid, it is generally preferred that the bottoms fraction contain between 1 and 20, most preferably between 5 and 15, weight percent water, and between 0.1 to 20, most preferably between 0.5 and 5, weight percent isopropyl acetate based on the total  
25 bottoms fraction. In this example, the bottoms fraction contains:

	Component	Weight Percent
	Acrylic Acid	81.8
	Water	10.0
	Acetic Acid	4.3
30	Formaldehyde	1.7
	Isopropyl Acetate	1.0
	Other (including dimer)	1.2

The bottoms fraction from dehydration column 216 is passed via line 230 to  
35 acid splitter column 232. The head pressure in acid splitter column is 0.093 bar and the

temperature is 50°C. The overhead from this column is cooled to 40°C for reflux and to pass to the solvent recovery column 238 via line 234. The base of the acid splitter column is maintained at 98°C. The bottoms fraction from acid splitter column 232 is passed via line 236 to finishing column 244.

- 5                   Returning to solvent recovery column 238, a head pressure of 0.33 bar absolute and a temperature of 60°C are maintained. The overhead is cooled to 40°C for both reflux and to return via line 240 to dehydration column 216. This overhead fraction contains:

	Component	Weight Percent
10	Isopropyl Acetate	81.3
	Water	15.7
	Acetic Acid	2.4
	Other	0.6

- 15                   The base of the solvent recovery column is maintained at 80°C. The bottoms fraction, which is primarily water, acetic acid and formaldehyde, is removed from the system via line 242. The high organic content of this stream enables it, if desired, to be consumed in, for example, steam boilers.

- 20                   In finishing column 244, which may be a flash column, the head is maintained at a temperature of 63°C with a pressure of 0.53 bar absolute. The overhead, which is cooled to 40°C for reflux and product withdrawal via line 248, contains 99.7 weight percent acrylic acid with the remaining components being primarily acetic acid and acrylic acid dimer. The base of the finishing column is at 110°C and the waste stream, which is withdrawn via line 246, contains 84 weight percent dimer of acrylic acid and 16 weight percent acrylic acid.

- 25                   Figures 1 and 3 depict a schematic process for the production of acetic acid from ethane. The cyclic loop is operated under substantially the same conditions as is the cyclic loop for the production of acrylic acid from propane described above. The catalyst is a mixed oxide catalyst having metal ratio of  $\text{Mo}_{61}\text{V}_{26}\text{Nb}_{7.2}\text{Sb}_{3.8}\text{Ca}_2$ , which is calcined at 350°C 5 for hours. 96 percent of the acetic acid produced is removed in separator 118.
- 30                   Since acetic acid does not polymerize, no polymerization inhibitor is maintained in absorber 124 or any of the vessels in the refining system.

A major difference between the processes is that in the production of acetic acid, little, if any, methanol, aldehydes and ketones are co-produced. Hence, the refining system is much less complex. Also, since acetic acid does not polymerize, the distillation

columns in the refining system can operate at pressures substantially above atmospheric.

With reference to Figure 3, the combined condensate stream and bottoms from the absorber 124 is passed to lites column 302 via line 122. The overhead is a vapor purge that exits the process via line 304 and may have sufficiently high fuel content to be used as fuel. The head  
5 pressure of lites column 302 is 4.5 bar absolute and the temperature is 58°C. The base temperature is 155 C.

The bottoms from lites column 302 is passed via line 314 to dehydration column 316 in which isopropyl acetate is used to form an azeotrope with water. The head of the dehydration column is maintained at 4.5 bar absolute and a temperature of 127 C. The  
10 base temperature is 175 C. From the base of dehydration column 316 is withdrawn glacial acetic acid via line 330.

The overhead from dehydration column 316 is contains primarily water and isopropyl acetate and is cooled to 40°C and then decanted in vessel 317. The upper fraction is returned as reflux and the lower fraction is passed via line 318 to heat exchanger 320  
15 which increases the temperature of the stream to 80°C. The heated stream is then passed via line 322 to solvent column 324 where isopropyl acetate is distilled from water. The head pressure in solvent column 324 is approximately ambient atmospheric pressure and the temperature is 93°C. The overhead from solvent column 324 is cooled to 40°C and decanted in vessel 326. The lower fraction is returned to the solvent column as reflux, and  
20 the upper fraction, which contains 97.5 weight percent isopropyl acetate and 2.5 weight percent water is returned via line 328 to dehydration column 316.

The bottoms fraction from solvent column 324, which is essentially water, is passed via line 350 through heat exchanger 320 where it is cooled from 100°C to 60°C. The stream is further cooled in heat exchanger 352 to 40°C and passed to splitter 354. Line 356  
25 from splitter 354 serves to purge water from the system to maintain a steady state operation. This purge stream is typically sent to waste water purification. The other portion of this stream is returned via line 126 to absorber 124 on Figure 1.

## CLAIMS:

1. A continuous process for catalytically oxidizing a hydrocarbyl reactant to carboxy compound of one or more of carboxylic acid and anhydride in which processes unreacted hydrocarbyl reactant is recycled in a cyclic loop is provided which comprises:
  - 5 a) continuously contacting in a vapor phase a gaseous mixture comprising containing hydrocarbyl reactant, an oxygen source and carbon oxides in the presence of a catalytically effective amount of a heterogeneous oxidation catalyst, under oxidation conditions to produce an effluent gas which contains carboxy compound and unreacted reactant and carbon oxides, wherein carbon oxides comprise at least 30 percent by  
10 volume of said gaseous mixture;
  - b) cooling said effluent gas to condense at least 50 percent of the carboxy compound and separating the condensed phase;
  - c) continuously recycling the effluent gas in the cyclic loop to step (a);
  - d) at least periodically withdrawing a purge from the cyclic loop said  
15 purge being in an amount sufficient to maintain steady state operation of the process; and
  - e) at least periodically adding to the cyclic loop sufficient amounts of hydrocarbyl reactant and oxygen to maintain steady-state operation.
2. The process of claim 1 wherein the hydrocarbyl reactant comprises aliphatic or aromatic hydrocarbon of 2 to 8 carbon atoms.
- 20 3. The process of claim 2 wherein the hydrocarbyl reactant comprises alkane of 2 to 8 carbon atoms.
4. The process of claim 3 wherein the hydrocarbyl reactant comprises ethane and the carboxy compound is acetic acid.
5. The process of claim 1 wherein the hydrocarbyl reactant contains a primary  
25 carbon and is an aliphatic or aromatic hydrocarbon of 2 to 8 carbon atoms and the carboxy compound is unsaturated.
6. The process of claim 5 wherein the hydrocarbyl reactant comprises propane and the carboxy compound is acrylic acid.
7. The process of claim 1 wherein at least 70 percent of the carboxy compound  
30 is condensed and separated in step b.
8. The process of claim 1 wherein the gaseous phase from the separation of step (b) is continuously contacted with an aqueous absorbent said contacting being under

conditions of temperature and pressure such that the aqueous absorbent selectively absorbs said carboxy compound as compared to said unreacted reactant.

9. The process of claim 1 wherein carbon oxides comprise 30 to 90 volume percent of the gases passed to step a.

5 10. The process of claim 1 wherein the hydrocarbyl reactant comprises 5 to 50 volume percent of the gases passed to step a.

11. The process of claim 10 wherein at least 60 percent of the oxygen passed to step a is reacted in a single pass.

10 12. The process of claim 1 wherein the hydrocarbyl reactant contains a primary carbon and is an aliphatic hydrocarbon of 3 to 5 carbon atoms; the carboxy compound is unsaturated and the cooling in step b is to a temperature below 50°C.

13. The process of claim 12 wherein step a is conducted at a pressure of between 4 and 30 bars absolute at a temperature between 225 and 555°C.

15 14. In a continuous processes for the catalytic oxidation of hydrocarbyl reactant to produce carboxy compound which comprises (a) reacting a hydrocarbyl reactant with an oxygen source in the presence of oxidation catalyst under oxidation conditions to produce a carboxy compound, carbon oxides and water; (b) separating said carboxy compound to provide a carboxy compound-rich stream and a carboxy compound-depleted stream; (c) recycling at least a portion of the carboxy compound-depleted stream to step (a); and (d)  
20 recovering carboxy compound from the separated carboxy compound-rich stream, the improvement comprising:

i) passing said separated carboxy compound-rich stream to a first distillation zone to produce a bottoms stream comprising less than 0.5 volume percent carbon oxides, and an overhead stream containing carbon oxides,

25 ii) passing the bottoms stream from the first distillation zone to a dehydration zone to produce a stream containing carboxy compound which stream is reduced in water content and contains less than 20 weight percent water.

16. The process of claim 15 wherein the dehydration zone comprises a  
30 dehydration distillation column.

17. The process of claim 16 wherein the dehydration of the stream containing carboxy compound is effected by azeotropic distillation.



18. The process of claim 17 wherein the hydrocarbyl reactant comprises alkane of 2 to 5 carbon atoms.
19. The process of claim 18 wherein the hydrocarbyl reactant comprises ethane and the carboxy compound is acetic acid.
- 5 20. The process of claim 18 wherein the hydrocarbyl reactant comprises propane and the carboxy compound is acrylic acid.

1 / 3

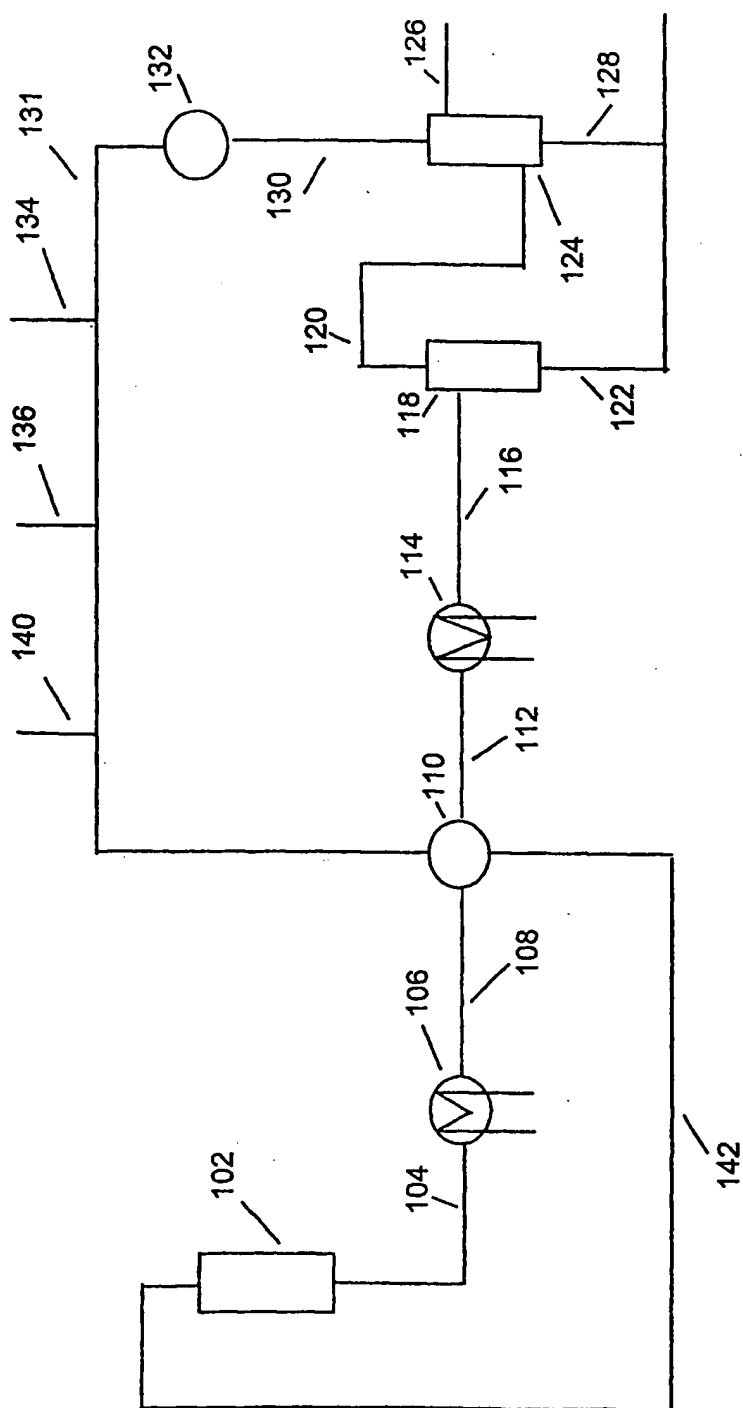


FIG. 1

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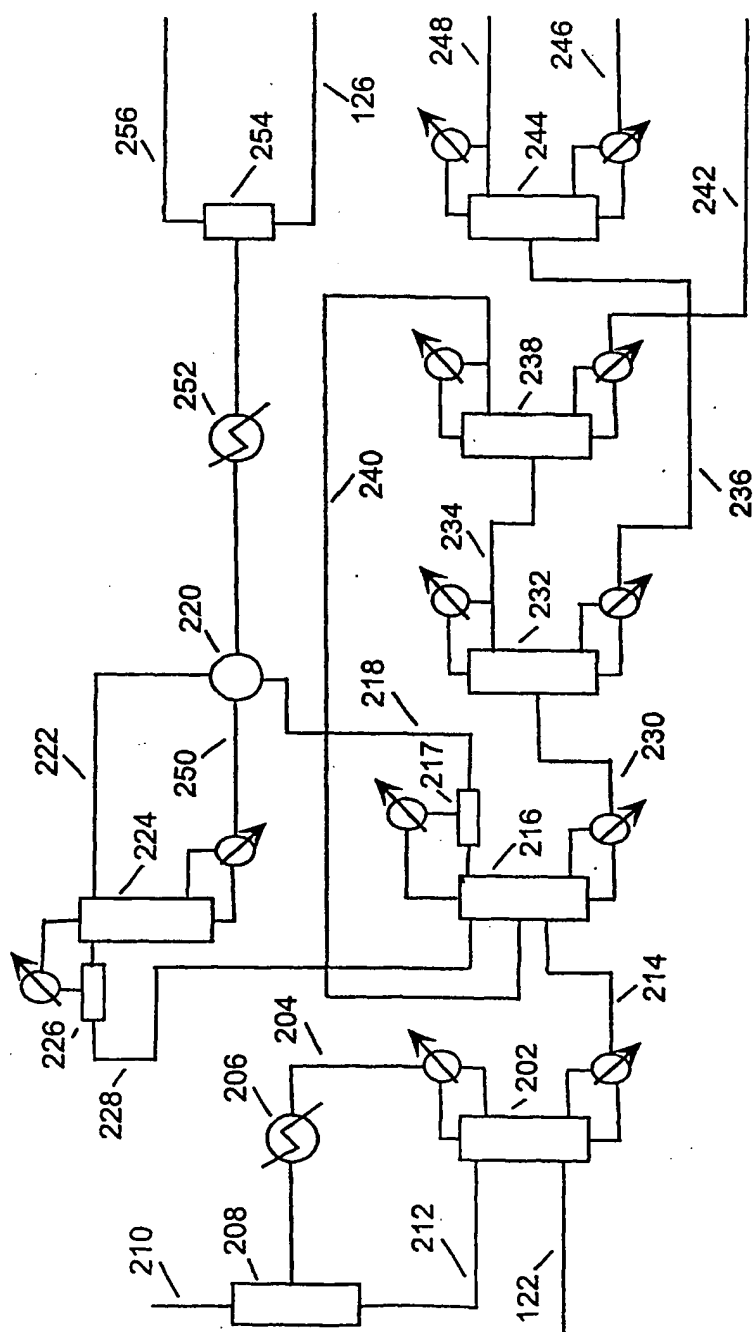


FIG. 2

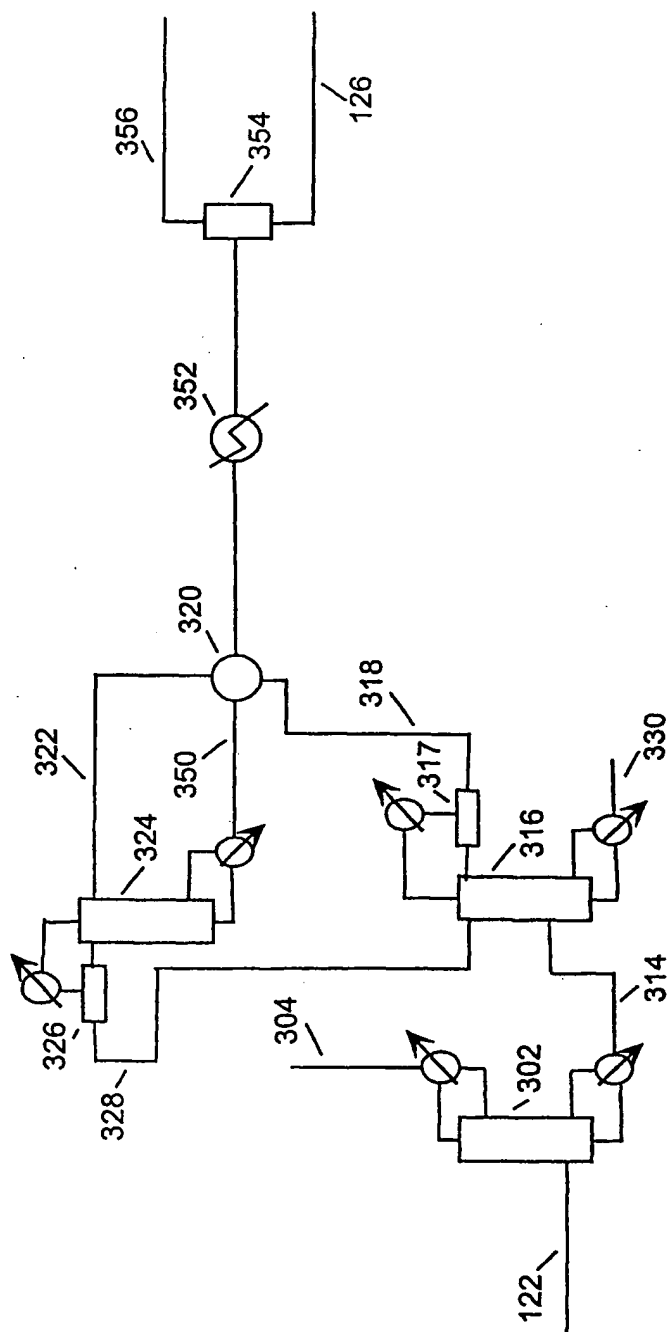


FIG. 3

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
18 April 2002 (18.04.2002)

PCT

(10) International Publication Number  
**WO 02/030861 A3**

(51) International Patent Classification<sup>7</sup>: C07C 51/215,  
53/08, 57/05, 51/44, 51/46

(21) International Application Number: PCT/US01/31320

(22) International Filing Date: 4 October 2001 (04.10.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
60/239,449 11 October 2000 (11.10.2000) US

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(81) Designated States (national): AE, AG, AL, AM, AT, AU,  
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CZ,  
DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM,  
HR, HU, ID, IL, IN, IS, JP, KE, KG, KR, KZ, LC, LK, LR,  
LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ,  
NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM,  
TR, TT, TZ, UA, UG, US, UZ, YU, ZA, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM,  
KE, LS, MW, MZ, SD, SI, SZ, TZ, UG, ZW), Eurasian  
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European  
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,  
IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF,  
CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD,  
TG).

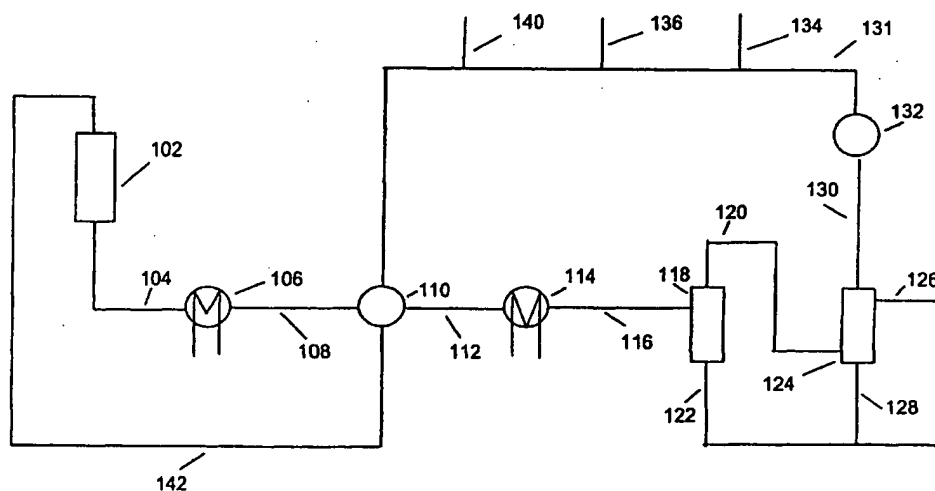
Published:

— with international search report

(88) Date of publication of the international search report:  
29 August 2002

For two-letter codes and other abbreviations, refer to the "Guid-  
ance Notes on Codes and Abbreviations" appearing at the begin-  
ning of each regular issue of the PCT Gazette.

(54) Title: PROCESSES FOR OXIDIZING HYDROCARBYL MOIETIES TO CARBOXYLIC ACIDS AND ANHYDRIDES



(57) Abstract: Continuous processes are provided for the partial oxidation in the vapor phase over a heterogeneous catalyst in a reaction zone of hydrocarbyl reactant to produce carboxylic acids or anhydrides wherein at least a portion of unreacted hydrocarbyl reactant is returned via a cyclic loop to the reaction zone. The partial oxidation generates carbon oxides which are used as ballast gas in the cyclic loop. The carboxylic acids or anhydrides are removed from the cyclic loop by condensation. Purification of the products can be by stripping lights and then dehydrating the carboxylic acid or anhydride product removed from the cyclic loop.

WO 02/030861 A3

## INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 01/31320

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07C51/215 C07C53/08 C07C57/05 C07C51/44 C07C51/46

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EP0-Internal

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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

24 May 2002

Date of mailing of the international search report

05/06/2002

Name and mailing address of the ISA

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## INTERNATIONAL SEARCH REPORT

Intern: Application No

PCT/US 01/31320

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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